

# First-principles study on the intermediate compounds of $\text{LiBH}_4$

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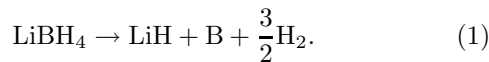
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We report the results of the first-principles calculation on the intermediate compounds of  $\text{LiBH}_4$ . The stability of  $\text{LiB}_3\text{H}_8$  and  $\text{Li}_2\text{B}_n\text{H}_n$  ( $n = 5-12$ ) has been examined with the ultrasoft pseudopotential method based on the density functional theory. Theoretical prediction has suggested that monoclinic  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  is the most stable among the candidate materials. We propose the following hydriding/dehydriding process of  $\text{LiBH}_4$  via this intermediate compound :  $\text{LiBH}_4 \leftrightarrow \frac{1}{12}\text{Li}_2\text{B}_{12}\text{H}_{12} + \frac{5}{6}\text{LiH} + \frac{13}{12}\text{H}_2 \leftrightarrow \text{LiH} + \text{B} + \frac{3}{2}\text{H}_2$ . The hydrogen content and enthalpy of the first reaction are estimated to be 10 mass% and 56 kJ/mol  $\text{H}_2$ , respectively, and those of the second reaction are 4 mass% and 125 kJ/mol  $\text{H}_2$ . They are in good agreement with experimental results of the thermal desorption spectra of  $\text{LiBH}_4$ . Our calculation has predicted that the bending modes for the  $\Gamma$ -phonon frequencies of monoclinic  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  are lower than that of  $\text{LiBH}_4$ , while stretching modes are higher. These results are very useful for the experimental search and identification of possible intermediate compounds.

## I. INTRODUCTION

Hydrogen is the most promising environmentally clean energy carrier to replace fossil fuels. The use of hydrogen-based energy in practical applications such as fuel cell vehicles, however, requires the development of safe and efficient hydrogen storage technology. Complex hydrides including the light metal lithium (Li) have sufficient gravimetric hydrogen storage capacity, and many researches and development about the lithium complex hydride such as  $\text{LiBH}_4$ <sup>1,2,3</sup> and  $\text{LiNH}_2$ <sup>4,5,6</sup> have been done recently. Particularly,  $\text{LiBH}_4$  can desorb about 14 mass% of hydrogen by the following thermal decomposition :



However, the experimental value of enthalpy of this reaction is 69 kJ/mol  $\text{H}_2$ <sup>1</sup> and  $\text{LiBH}_4$  is too stable to release hydrogen at ambient condition. High temperature and high pressure are needed for rehydriding reaction, so its reversibility becomes a problem for practical use.

Züttel *et al.*<sup>1</sup> investigated the hydrogen desorption from  $\text{LiBH}_4$  in details, and reported that the thermal desorption spectra of  $\text{LiBH}_4$  mixed with  $\text{SiO}_2$ -powder exhibited three hydrogen desorption peaks. These peaks were observed around 500 K, 550 K and 600 K, and the products corresponded to “ $\text{LiBH}_{3.6}$ ”, “ $\text{LiBH}_3$ ” and “ $\text{LiBH}_2$ ”, respectively. The compounds in quotes were nominal compositions estimated from amount of desorbed hydrogen. This is a strong evidence for the existence of the intermediate compounds, and the hydrogen desorption reaction takes place in at least two steps not a single step like in Eq.(1). Although low temperature release of hydrogen and improvement of reversibility can be expected

by use of the intermediate compound, little attention has been paid yet.

In this study, the stability of the intermediate compounds of  $\text{LiBH}_4$  has been investigated theoretically and we clarify a hydriding/dehydriding process of  $\text{LiBH}_4$ . The thermal desorption experiment observed a structural transition around 380 K and the melting of the compound at 550 K. The stability of the solid phases at absolute zero temperature is mainly discussed here. In Sec. II, we describe the details of the computational method and the possible intermediate compounds of  $\text{LiBH}_4$ . Section III reports the calculated results on the stability of some candidate compounds. And then, we discuss the hydriding/dehydriding reaction via the intermediate compounds. Furthermore, the electronic structures and  $\Gamma$ -phonon frequencies on the most stable compound are studied. We also investigate the stability of the borane complex anions, and then compare with the solid compounds.

## II. COMPUTATIONAL DETAILS

First-principles calculations have been performed by the ultrasoft pseudopotential method<sup>7</sup> based on the density functional theory.<sup>8</sup> The generalized gradient approximation (GGA) formula<sup>9</sup> is applied to the exchange-correlation energy.

The interaction between the ion cores and electrons is described by the ultrasoft pseudopotential<sup>7</sup>, and the norm-conservation constraint<sup>10</sup> is imposed on Li for the calculation efficiency improvement. The scalar-relativistic all-electron calculations are first carried out on the free atoms(ions). We chose 2s and 2p states for

both Li and B pseudopotential as the reference states with the cutoff radii of 2 a.u. (Li) and 1.5 a.u. (B), respectively. A single projector function is used for each angular momentum component. The  $3d$  state is treated as the local part of pseudopotential. The hydrogen pseudopotential is constructed from  $1s, 2s$  and  $2p$  states with the cutoff radii of 1.1 a.u.( $s$ ) and 1.2 a.u. ( $p$ ). We use double projector functions for the  $s$  component and a single projector function for the  $p$  component. For all pseudopotentials, the pseudo-wave functions and the pseudo-charge-augmentation functions are optimized by a method similar to that proposed by Rappe *et al.*<sup>11</sup> Also, the partial core correction<sup>12</sup> is taken into account for Li and B pseudopotentials.

In the solid-state calculations, the pseudo-wave functions are expanded by plane waves with a cutoff energy equal to 15 hartrees. The cutoff energy for the charge density and potential is set to be 120 hartrees. The integral over the Brillouin zone is approximated by the summation on the  $\mathbf{k}$ -grid elements of which the edge lengths closer to the target value of  $0.15\text{\AA}^{-1}$  as possible. We confirmed that these calculation conditions gave a good convergence of energy within 0.002 eV/atom. The preconditioned conjugate-gradient technique is employed to minimize the Kohn-Sham energy functional. A procedure based on the iterative diagonalization scheme<sup>13</sup> and the Broyden charge mixing method<sup>14</sup> is adopted in this study. Optimization of crystal structures is performed till the atomic forces and the macroscopic stresses become less than  $5 \times 10^{-4}$  hartree/bohr and 0.1 GPa, respectively. During the structural optimization process, the partial occupation numbers near the Fermi level are determined by the Fermi-Dirac distribution function with  $k_B T = 3 \times 10^{-3}$  hartrees. The Helmholtz free-energy functional,<sup>15</sup> including the entropy term, is minimized instead of the Kohn-Sham energy functional. Then, the improved tetrahedron method<sup>16</sup> is used in order to minimize the Kohn-Sham energy functional in the optimized structure. The dynamical matrix is calculated by the force-constant method<sup>17</sup> to obtain the  $\Gamma$  phonon frequencies. The atomic displacement is set to be 0.02 Å. The further details of calculation are described in Refs. 2, 13 and references therein.

As the candidates of the intermediate compounds, the existing alkali metal-B-H materials are used. For example, it is well known that boron (B) and hydrogen (H) form inorganic compounds called 'borane' and the compounds of  $\text{CsB}_3\text{H}_8$ ,<sup>18</sup>  $\text{K}_2\text{B}_6\text{H}_6$ ,<sup>19</sup> and  $\text{K}_2\text{B}_{12}\text{H}_{12}$ <sup>20</sup> are reported. The space group of crystal structure for the compound  $\text{CsB}_3\text{H}_8$  is  $Ama2$  (No.40) and cation  $\text{Cs}^+$  and anion  $[\text{B}_3\text{H}_8]^-$  are arranged same as the NaCl-type structure with an orthorhombic distortion. The crystal structures of  $\text{K}_2\text{B}_6\text{H}_6$  and  $\text{K}_2\text{B}_{12}\text{H}_{12}$  are best described as an anti- $\text{CaF}_2$ -type arrangement with  $\text{K}^+$  cation in the center of a tetrahedron formed by  $[\text{B}_n\text{H}_n]^{2-}$  dianions. We first assumed that  $\text{LiB}_3\text{H}_8$ ,  $\text{Li}_2\text{B}_6\text{H}_6$  and  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  compounds, which had the same crystal structures as existing  $\text{CsB}_3\text{H}_8$ ,  $\text{K}_2\text{B}_6\text{H}_6$  and  $\text{K}_2\text{B}_{12}\text{H}_{12}$ , respectively. The

stability of these candidates was evaluated using the first-principles calculations. Since the existence of a series of *closo*-type dianions  $[\text{B}_n\text{H}_n]^{2-}$  ( $n = 5 - 12$ ) is also well known, our calculation have been expanded to  $\text{Li}_2\text{B}_n\text{H}_n$  ( $n = 5 - 12$ ) compounds. Although Li atom and  $[\text{B}_n\text{H}_n]$  cluster are arranged in the anti- $\text{CaF}_2$ -type structure and the unit cell parameters are supposed to be a face-centered-cubic symmetry ( $a = b = c, \alpha = \beta = \delta = 90^\circ$ ) as starting points for the structural optimization, the output relaxed compounds have different symmetry depending on the structure of  $[\text{B}_n\text{H}_n]$  clusters. The alkali metal salt of monoclinic  $\text{K}_2\text{B}_{12}(\text{OH})_{12}$ <sup>21</sup> with *closo*- $[\text{B}_{12}(\text{OH})_{12}]^{2-}$  dianions has been reported, and monoclinic  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  with similar crystal structure is also examined.

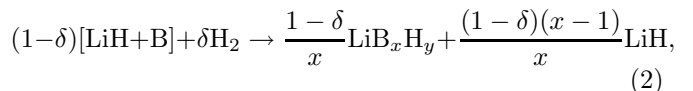
### III. RESULTS AND DISCUSSIONS

#### A. Stability of candidate compounds : $\text{LiB}_x\text{H}_y$

Table I shows the calculated results on the structural parameters and the cohesive energies of  $\text{LiB}_3\text{H}_8$  and  $\text{Li}_2\text{B}_n\text{H}_n$  ( $n = 5 - 12$ ). We denote the cubic  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  based on  $\text{K}_2\text{B}_{12}\text{H}_{12}$  with type-1 and monoclinic  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  based on  $\text{K}_2\text{B}_{12}(\text{OH})_{12}$  with type-2, respectively. Compared with the cohesive energy of two type of  $\text{Li}_2\text{B}_{12}\text{H}_{12}$ , the value of monoclinic  $\text{Li}_2\text{B}_{12}\text{H}_{12}$ (type-2) is larger than that of type-1. Therefore, the type-2  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  is easy to form. After the next paragraph, the only result concerning monoclinic  $\text{Li}_2\text{B}_{12}\text{H}_{12}$ (type-2) is shown.

The enthalpy of formation for hydriding reactions including  $\text{LiBH}_4$  from  $\text{LiH}$  (NaCl-type),  $\alpha$ -B (rhombohedral), and  $\text{H}_2$  molecule are given in Table II, where the zero-point energy corrections are not taken into consideration. They are provided using calculated cohesive energies of 2.3609 eV/atom for  $\text{LiH}$ , 6.2013 eV/atom for  $\alpha$ -B, 2.2689 eV/atom for  $\text{H}_2$  molecule, and 3.1501 eV/atom for  $\text{LiBH}_4$ (orthorhombic  $Pnma$  symmetry), respectively. The enthalpies of formation for  $\text{Li}_2\text{B}_n\text{H}_n$  ( $n = 10, 11, 12$ ) are more negative than that for  $\text{LiBH}_4$ . Therefore these compounds have a great potential for generating in hydriding reactions from  $\text{LiH}$  and  $\alpha$ -B as the intermediate phase of  $\text{LiBH}_4$ .

In order to understand the stability of each compound intuitively, we represent the enthalpy of formation corresponding to the following reaction with hydrogen of  $\delta$  mole in Fig. 1 :



where  $\delta = (y-1)/(2x+y-1)$  shows the mole fraction of  $\text{H}_2$  and  $x \geq 1$ . From Fig. 1, monoclinic  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  is formed as the intermediate compound of the hydriding/dehydriding reaction of  $\text{LiBH}_4$ , because the actual reaction goes along the lowest state of enthalpy. Therefore, following hydriding/dehydriding process is proposed

TABLE I: Structural parameters and cohesive energies ( $E_{coh}$ ) of the candidate compounds :  $\text{LiB}_x\text{H}_y$ . It is denoted that the cubic  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  based on  $\text{K}_2\text{B}_{12}\text{H}_{12}$  with type-1 and monoclinic  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  based on  $\text{K}_2\text{B}_{12}(\text{OH})_{12}$  with type-2, respectively.

Compound	Space group	Unit cell parameters	Atomic position					$E_{coh}$ (eV/atom)
			Atom	Site	$x/a$	$y/b$	$z/c$	
$\text{LiB}_3\text{H}_8$	$Ama2$ ( $No.40$ )	$a = 9.188 \text{ \AA}$ $b = 8.813 \text{ \AA}$ $c = 5.763 \text{ \AA}$	Li	4b	0.0595	0.6321	0.25	3.3770
			B1	4b	0.1372	0.1335	0.25	
			B2	8c	0.3090	0.1331	0.0945	
			H1	4b	0.0690	0.2507	0.25	
			H2	4b	0.0684	0.1666	0.25	
			H3	8c	0.1386	0.5149	0.5190	
			H4	8c	0.1823	0.1333	0.0063	
			H5	8c	0.3619	0.2508	0.0186	
$\text{Li}_2\text{B}_5\text{H}_5$	$R3m$ ( $No.160$ ) (hexagonal axes)	$a = 5.599 \text{ \AA}$ $c = 16.763 \text{ \AA}$	Li1	3a	0	0	0.2755	3.7910
			Li2	3a	0	0	0.7513	
			B1	3a	0	0	0.0876	
			B2	3a	0	0	0.9295	
			B3	9b	0.1070	0.8930	0.0084	
			H1	3a	0	0	0.1595	
			H2	3a	0	0	0.8586	
			H3	9b	0.2270	0.7730	-0.0078	
$\text{Li}_2\text{B}_6\text{H}_6$	$Fm\bar{3}m$ ( $No.225$ )	$a = 7.968 \text{ \AA}$	Li	8c	0.25	0.25	0.25	4.0429
			B	24e	0.1553	0	0	
			H	24e	0.3054	0	0	
$\text{Li}_2\text{B}_7\text{H}_7$	$I2$ ( $No.5$ )	$a = 5.691 \text{ \AA}$ $b = 9.836 \text{ \AA}$ $c = 5.625 \text{ \AA}$ $\beta = 77.39^\circ$	Li1	2b	0	0.1501	0.5	4.0850
			Li2	2b	0.5	0.2317	0	
			B1	2a	0	0.1564	0	
			B2	4c	-0.1871	0.0529	-0.1063	
			B3	4c	0.1160	-0.1087	0.0659	
			B4	4c	-0.1335	0.0087	0.1903	
			H1	2a	0	0.2792	0	
			H2	4c	-0.3463	0.0805	-0.2099	
$\text{Li}_2\text{B}_8\text{H}_8$	$I\bar{4}2m$ ( $No.121$ )	$a = 5.572 \text{ \AA}$ $c = 10.687 \text{ \AA}$	H3	4c	0.2215	-0.2030	0.1343	4.0920
			H4	4c	-0.2700	0.0109	0.3879	
			Li	4d	0	0.5	0.25	
			B1	8i	0.1032	0.1032	-0.1242	
			B2	8i	0.1631	0.1631	0.0304	
			H1	8i	0.2031	0.2031	-0.2112	
			H2	8i	0.3114	0.3114	0.0580	
			Li1	3a	0	0	0.2482	4.1326
$\text{Li}_2\text{B}_9\text{H}_9$	$R3$ ( $No.146$ ) (hexagonal axes)	$a = 7.044 \text{ \AA}$ $c = 15.062 \text{ \AA}$	Li2	3a	0	0	0.8070	
			B1	9b	0.8087	0.9031	0.9508	
			B2	9b	0.8118	0.9047	0.0694	
			B3	9b	0.8661	0.7287	0.0096	
			H1	9b	0.6730	0.8346	0.8923	
			H2	9b	0.6756	0.8357	0.1281	
			H3	9b	0.7699	0.5322	0.0141	
$\text{Li}_2\text{B}_{10}\text{H}_{10}$	$I422$ ( $No.97$ )	$a = 6.196 \text{ \AA}$ $c = 10.356 \text{ \AA}$	Li	4d	0	0.5	0.25	4.2360
			B1	4e	0	0	0.1827	
			B2	16k	0.1942	-0.0809	0.0739	
			H1	4e	0	0	0.2984	
			H2	16k	0.3647	-0.1582	0.1070	
			Li1	2b	0	-0.1091	0.5	4.2397
$\text{Li}_2\text{B}_{11}\text{H}_{11}$	$I2$ ( $No.5$ )	$a = 7.083 \text{ \AA}$ $b = 11.028 \text{ \AA}$ $c = 7.080 \text{ \AA}$ $\beta = 70.52^\circ$	Li2	2b	0.5	-0.1083	0	
			B1	2a	0	-0.1264	0	
			B2	4c	0.1117	0.1190	-0.1120	
			B3	4c	0.0835	-0.0162	-0.2427	
			B4	4c	0.2425	-0.0162	-0.0840	
			B5	4c	0.1293	0.0825	0.1290	
			B6	4c	0.1448	-0.0795	0.1446	
			H1	2a	0	-0.2355	0	
			H2	4c	0.2016	0.2052	-0.2020	
			H3	4c	0.4160	-0.0284	-0.1910	
			H4	4c	0.1902	-0.0283	-0.4165	
			H5	4c	0.2133	0.1471	0.2127	
			H6	4c	0.2305	-0.1441	0.2300	
$\text{Li}_2\text{B}_{12}\text{H}_{12}$ (type-1)	$Fm\bar{3}$ ( $No.202$ )	$a = 10.083 \text{ \AA}$	Li	8c	0.25	0.25	0.25	4.2997
			B	48h	0	0.1448	0.0881	
			H	48h	0	0.2490	0.1469	
$\text{Li}_2\text{B}_{12}\text{H}_{12}$ (type-2)	$P2_1/n$ ( $No.14$ )	$a = 7.358 \text{ \AA}$ $b = 9.556 \text{ \AA}$ $c = 6.768 \text{ \AA}$ $\beta = 92.26^\circ$	Li	4e	0.6747	0.6250	0.5323	4.3461
			B1	4e	0.6770	0.5392	0.1632	
			B2	4e	0.4447	0.5629	0.2239	
			B3	4e	0.5425	0.6760	0.0442	
			B4	4e	0.6915	0.5689	0.9022	
			B5	4e	0.6856	0.3922	0.9959	
			B6	4e	0.5329	0.3887	0.1933	
			H1	4e	0.8033	0.5642	0.2786	
			H2	4e	0.4008	0.6050	0.3840	
			H3	4e	0.5707	0.7983	0.0742	
			H4	4e	0.8252	0.6151	0.8271	
			H5	4e	0.8231	0.3231	0.9941	
			H6	4e	0.5558	0.3097	0.3310	

TABLE II: The enthalpies of formation for the hydriding reaction of various compounds  $\text{LiB}_x\text{H}_y$  including  $\text{LiBH}_4$  from  $\text{LiH}$ ,  $\alpha\text{-B}$ , and  $\text{H}_2$  molecule, where the zero-point energy corrections are not taken into consideration.

Hydriding reaction	Enthalpy of formation (kJ/mol $\text{H}_2$ )
$\text{LiH} + 3\text{B} + 7/2\text{H}_2 \rightarrow \text{LiB}_3\text{H}_8$	-36
$2\text{LiH} + 5\text{B} + 3/2\text{H}_2 \rightarrow \text{Li}_2\text{B}_5\text{H}_5$	113
$2\text{LiH} + 6\text{B} + 2\text{H}_2 \rightarrow \text{Li}_2\text{B}_6\text{H}_6$	-42
$2\text{LiH} + 7\text{B} + 5/2\text{H}_2 \rightarrow \text{Li}_2\text{B}_7\text{H}_7$	-45
$2\text{LiH} + 8\text{B} + 3\text{H}_2 \rightarrow \text{Li}_2\text{B}_8\text{H}_8$	-32
$2\text{LiH} + 9\text{B} + 7/2\text{H}_2 \rightarrow \text{Li}_2\text{B}_9\text{H}_9$	-42
$2\text{LiH} + 10\text{B} + 4\text{H}_2 \rightarrow \text{Li}_2\text{B}_{10}\text{H}_{10}$	-87
$2\text{LiH} + 11\text{B} + 9/2\text{H}_2 \rightarrow \text{Li}_2\text{B}_{11}\text{H}_{11}$	-79
$2\text{LiH} + 12\text{B} + 5\text{H}_2 \rightarrow \text{Li}_2\text{B}_{12}\text{H}_{12}$	-125
$\text{LiH} + \text{B} + 3/2\text{H}_2 \rightarrow \text{LiBH}_4$	-75

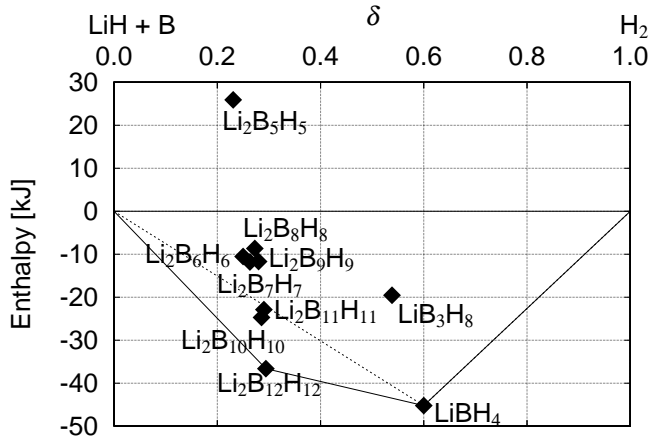
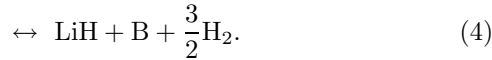
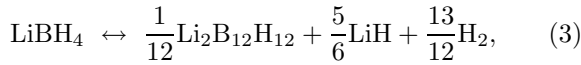


FIG. 1: Enthalpy of formation relative to  $(1 - \delta)[\text{LiH} + \text{B}]$  and molecular  $\text{H}_2$  of  $\delta$  mole (reaction Eq.(2) in text), as a function of the mole fraction of  $\text{H}_2$ ,  $\delta$ .

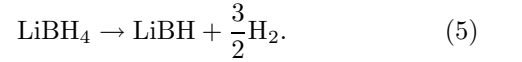
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The enthalpy without zero-point energy effects and hydrogen content of the first reaction (Eq.(3)) are 56 kJ/mol  $\text{H}_2$  and 10 mass% and those of the second reaction (Eq.(4)) are 125 kJ/mol  $\text{H}_2$  and 4 mass%, respectively. These results agree with the experimental ones, which reported that 9 mass% of hydrogen are liberated in the hydrogen desorption peak in thermal desorption spectra of  $\text{LiBH}_4$  mixed with  $\text{SiO}_2$ -powder in Ref. 1. The enthalpy value of 56 kJ/mol  $\text{H}_2$  for the first reaction is lower than computational one of 75 kJ/mol  $\text{H}_2$  for direct dehydriding reaction of  $\text{LiBH}_4$  (Eq.(1)).<sup>2</sup> So the hydrogen desorption and absorption can occur at low temperature and pressure comparatively by using this intermediate compound.

We also calculated other possible crystal structures such as  $\text{Cu}_2\text{B}_{10}\text{H}_{10}$ -type<sup>22</sup> and  $[\text{Li}(\text{thp})_3]_2[\text{B}_{11}\text{H}_{11}]$ -type.<sup>23</sup> Moreover, we performed the calculation for the  $\Gamma$ -phonon frequencies of the candidate materials. If there was a soft-mode, we lowered crystal structure symmetry with moving the atoms along the direction of the soft-mode eigenvectors. The maximum gain of cohesive energy was 0.03 eV/atom for  $\text{Li}_2\text{B}_6\text{H}_6$ , however, no compound or crystal structure more stable than monoclinic  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  was found. The present calculation result on the energy of monoclinic  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  provides the upper limit value for the thermodynamic stability. In conclusion, the existence of the intermediate compound of  $\text{LiBH}_4$  was predicted theoretically.

Recently Kang *et al.*<sup>24</sup> have reported that  $\text{LiBH}$  and  $\text{LiB}$  are the intermediate phases of  $\text{LiBH}_4$ , and propose the dehydriding reaction of  $\text{LiBH}_4$  through  $\text{LiBH}$  as follows :



We also performed the first-principles calculation of the orthorhombic phase of  $Pnma$   $\text{LiBH}$ . The reaction enthalpy for Eq.(5) is 1.30eV per  $\text{LiBH}_4$  formula unit (84kJ/mol $\text{H}_2$ ), which is in good agreement with reported value of 1.28eV per  $\text{LiBH}_4$  formula unit in Ref.24. On the other hand, the reaction enthalpy of Eq.(3) is 0.63eV per  $\text{LiBH}_4$  formula unit. Therefore, the dehydriding reaction via the intermediate compound  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  is energetically more preferable one.

## B. Intermediate compound : $\text{Li}_2\text{B}_{12}\text{H}_{12}$

Here we describe the fundamental properties, such as the crystal structure, the electronic structure, and the  $\Gamma$  phonon frequencies, on  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  which is expected as intermediate compound of  $\text{LiBH}_4$ .

Optimized crystal structure model of monoclinic  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  is shown in Fig. 2. The bond lengths between B and H atom of  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  are 1.20 – 1.21 Å, and they are very close to those for  $\text{LiBH}_4$  (1.23 – 1.24 Å) reported in Ref. 2. As for the B-B bond lengths of intra-icosahedron, the values of 1.779 – 1.811 Å for  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  are comparable to the experimental ones for the  $\alpha$ -rhombohedral boron ( $\alpha\text{-B}$ ) of 1.751 – 1.806 Å,<sup>25</sup> too. Since boron crystal has the icosahedral  $\text{B}_{12}$  cluster as a common structural component, the decomposition of  $[\text{B}_{12}\text{H}_{12}]^{2-}$  anion into  $\text{B}_{12}$  cluster and hydrogen molecule is easy to understand.

Figure 3 shows the total and partial density of states (DOS) for  $\text{Li}_2\text{B}_{12}\text{H}_{12}$ , which denotes that it has the energy gap of 5.60 eV. Since there is little contribution of Li orbital for occupied states,  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  consists of  $\text{Li}^+$  and  $[\text{B}_{12}\text{H}_{12}]^{2-}$  ions. The orbitals of B and H hybridize each other and the feature of occupied states in DOS is analogous with the distribution of the computed energies of the bonding molecular orbitals in  $[\text{B}_{12}\text{H}_{12}]^{2-}$ .<sup>26</sup>

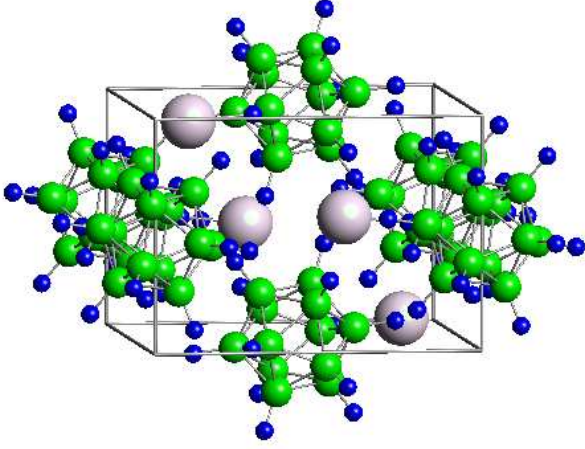


FIG. 2: (Color online) Crystal structure model of monoclinic  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  (type-2). Large, middle, and small spheres denote Li, B, and H atoms, respectively.

The  $\Gamma$ -phonon mode frequencies of monoclinic  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  have been calculated so that the vibrational properties can be compared with experiments easily and directly. The phonon density of states is shown in Fig. 4. It is divided into three regions in the same case as  $\text{LiBH}_4$ . The first region is less than  $300\text{ cm}^{-1}$  where the displacements of Li atoms are dominant. The second region is between  $450\text{ cm}^{-1}$  and  $1100\text{ cm}^{-1}$  where the B-H bond of  $[\text{B}_{12}\text{H}_{12}]^{2-}$  dianions vibrates with changing in angle between them (bending modes), and the third region is between  $2400\text{ cm}^{-1}$  and  $2600\text{ cm}^{-1}$  where the interatomic distance of B-H bond is changing along bond axis (stretching modes). The frequencies of bending modes are lower than  $\text{LiBH}_4$  described in Ref. 2, while stretching modes are higher.

The investigation using in situ Raman spectroscopy is effective for the confirmation of the short-range order or bonding of  $\text{LiBH}_4$ .<sup>27</sup> We examine the atomistic vibrations of  $\text{LiBH}_4$  during heating by in situ Raman spectroscopy, and the identification of spectra modes originating from  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  is now in progress.<sup>28</sup>

### C. Stability of complex anions : $[\text{B}_n\text{H}_n]^{2-}$

Finally, we consider the relation between the stability of the compounds  $\text{Li}_2\text{B}_n\text{H}_n$  and those of complex anions  $[\text{B}_n\text{H}_n]^{2-}$ . The energies of the isolated  $[\text{B}_n\text{H}_n]^{2-}$  are obtained using a face-centered-cubic supercell with  $a = 20\text{ \AA}$ . The single  $\Gamma$  point is used for the  $\mathbf{k}$ -point sampling. The energies for the charged systems are computed by adding uniform background charges and improved with Makov and Payne correction<sup>29</sup> for the interaction between periodic image charges.

Figure 5 shows the comparison of the formation energies,  $E_f^{\text{solid}}$  and  $E_f^{\text{complex}}$ , corresponding to the following

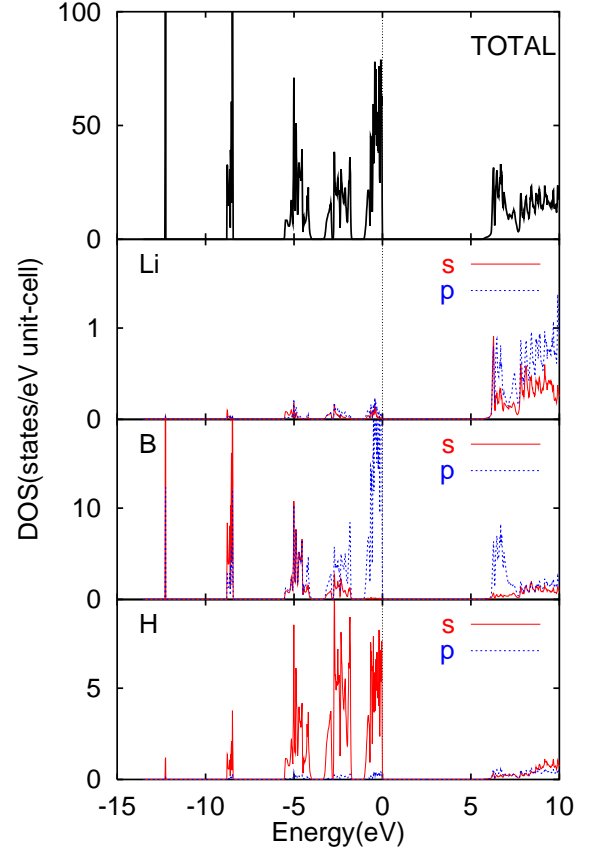


FIG. 3: (Color online) The total and partial densities of states (DOS) for  $\text{Li}_2\text{B}_{12}\text{H}_{12}$ . The energy is measured in eV relative to the top of valence states.

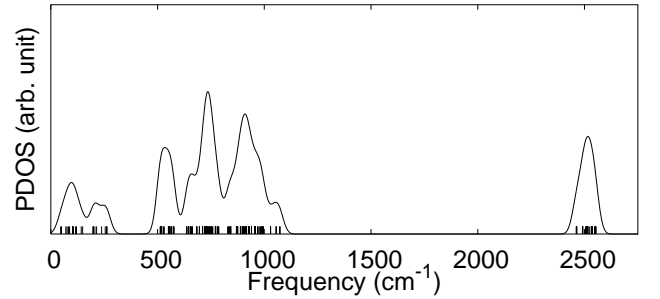
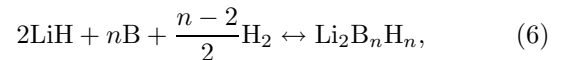


FIG. 4: Phonon density of states for monoclinic  $\text{Li}_2\text{B}_{12}\text{H}_{12}$ . The contribution of the TO  $\Gamma$ -phonon modes indicated by vertical bars is only taken into account and the Gaussian broadening with a width of  $30\text{ cm}^{-1}$  is used.

reactions:



and



where the energies are normalized by the number of B-H pairs for comparison purposes. We can find a fairly good

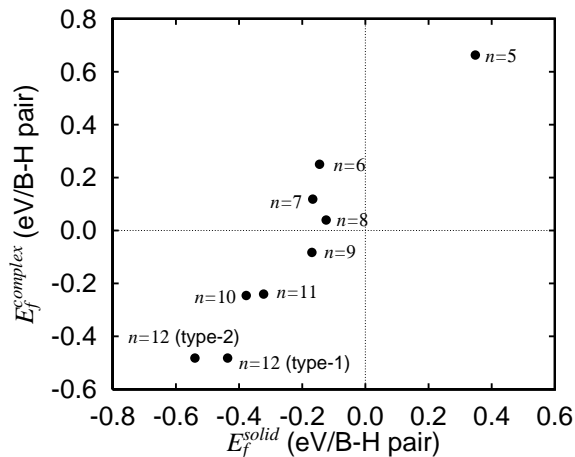


FIG. 5: Comparison of the formation energies,  $E_f^{solid}$  and  $E_f^{complex}$ , corresponding to the reactions Eq.(6) and Eq.(7) in text, respectively, where the energies are normalized by the number of B-H pairs.

correlation between both energies. This is probably due to the fact that the electrostatic interaction between  $\text{Li}^+$  and  $[\text{B}_n\text{H}_n]^{2-}$  is not sensitive to  $n$  and a large part of this energy cancels out with that of  $\text{LiH}$  in Eq. (6). Among the *closo*-type dianions considered here,  $[\text{B}_{12}\text{H}_{12}]^{2-}$  is the most stable one.

$\text{LiBH}_4$  desorbs hydrogen at temperatures above the melting point. The latent heat of fusion has been reported<sup>30</sup> to be 0.078 eV/formula-unit for  $\text{LiBH}_4$  and similar values are expected for  $\text{Li}_2\text{B}_n\text{H}_n$ , which is considerably smaller than the energy difference between  $[\text{B}_{12}\text{H}_{12}]^{2-}$  and other *close*-type dianions. The stability of the  $[\text{B}_{12}\text{H}_{12}]^{2-}$  anion supports our main conclusion in this study, that is, the intermediate phase suggested by the experiment is  $\text{Li}_2\text{B}_{12}\text{H}_{12}$ .

#### IV. SUMMARY

We have examined the stability of  $\text{LiB}_3\text{H}_8$  and  $\text{Li}_2\text{B}_n\text{H}_n$  ( $n = 5 - 12$ ), which are the possible intermediate compounds of  $\text{LiBH}_4$ , by the first-principles calculation. Our computational results for enthalpy of the hydriding reactions provide that monoclinic  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  is the most stable one among the candidates. The follow-

ing hydriding/dehydriding process of  $\text{LiBH}_4$  is proposed :  $\text{LiBH}_4 \leftrightarrow 1/12\text{Li}_2\text{B}_{12}\text{H}_{12} + 5/6\text{LiH} + 13/12\text{H}_2 \leftrightarrow \text{LiH} + \text{B} + 3/2\text{H}_2$ . The hydrogen content of the first and the second reaction are 10 mass% and 4 mass%, respectively, which agree well with the thermal desorption spectra (TDS) experiment on  $\text{LiBH}_4$ .<sup>1</sup> The heat of formation without zero point energy corrections for the first reaction, which is estimated from the solid state  $\text{LiBH}_4$  with *Pnma* symmetry (not liquid  $\text{LiBH}_4$ ), is 56 kJ/mol $\text{H}_2$ . This value is lower than that for the direct reaction ( $\text{LiBH}_4 \leftrightarrow \text{LiH} + \text{B} + \frac{3}{2}\text{H}_2$ ). Therefore, low temperature release of hydrogen can be expected by use of this intermediate compound.

We have calculated the electronic structure and the  $\Gamma$ -phonon frequencies of monoclinic  $\text{Li}_2\text{B}_{12}\text{H}_{12}$ . This compound has the energy gap of 5.60 eV and consists of  $\text{Li}^+$  and  $[\text{B}_{12}\text{H}_{12}]^{2-}$  ions. From the phonon density of states, it is predicted that its bending modes have lower frequencies than that of  $\text{LiBH}_4$ ,<sup>2</sup> while stretching modes are higher. The identification of the experimental Raman spectra modes originating from  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  is now in progress.

The stability of *closo* borane complex anions  $[\text{B}_n\text{H}_n]^{2-}$  was also examined. We found a fairly good correlation between the formation energies of the solid phases and the isolated dianions. This result supports the validity of the intermediate compound indicated in the TDS experiment being  $\text{Li}_2\text{B}_{12}\text{H}_{12}$ .

There are various kinds of borane, such as *nido*-type  $[\text{B}_n\text{H}_{n+4}]$  and *arachno*-type  $[\text{B}_n\text{H}_{n+6}]$ , in addition to *closo*-type borane  $[\text{B}_n\text{H}_{n+2}]$ .<sup>31</sup> The *nido* and *arachno* borane are derived from *closo* borane by removing one and two vertices, respectively. These generate the salts in the ionized state as well as *closo*-type dianions. These alkali metal salts are also the candidates of the intermediate compound of  $\text{LiBH}_4$ . We will study the details of the hydriding/dehydriding process for  $\text{LiBH}_4$  including the stability of these materials in future.

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<sup>1</sup> A. Züttel, P. Wenger, S. Rentsch, P. Sudan, Ph. Mauron, and Ch. Emmenegger, J. Power Sources **118**, 1 (2003).

<sup>2</sup> K. Miwa, N. Ohba, S. Towata, Y. Nakamori, and S. Orimo, Phys. Rev. B **69**, 245120 (2004).

<sup>3</sup> S. Orimo, Y. Nakamori, and A. Züttel, Mater. Sci. Eng. B **108**, 51 (2004).

<sup>4</sup> P. Chen, Z. Xiong, J. Luo, J. Lin, and K. L. Tan, Nature

**420**,302 (2002).

<sup>5</sup> Y. Nakamori and S. Orimo, Mater. Sci. Eng. B **108**, 48 (2004).

<sup>6</sup> K. Miwa, N. Ohba, S. Towata, Y. Nakamori, and S. Orimo, Phys. Rev. B **71**, 195109 (2005).

<sup>7</sup> D. Vanderbilt, Phys. Rev. B **41**, R7892 (1990); K. Laasonen, A. Pasquarello, R. Car, C. Lee, and D. Vanderbilt,

- ibid.* **47**, 10 142 (1993).
- <sup>8</sup> P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
  - <sup>9</sup> J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); **78**, 1396 (E) (1997).
  - <sup>10</sup> D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979) .
  - <sup>11</sup> A. M. Rappe, K. M. Rabe, E. Kaxiras, and J. D. Joannopoulos, Phys. Rev. B **41**, 1227 (1990) .
  - <sup>12</sup> S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**, 1738 (1982) .
  - <sup>13</sup> A. Fukumoto and K. Miwa, Phys. Rev. B **55**, 11 155 (1997) .
  - <sup>14</sup> V. Eyret, J. Comput. Phys. **124**, 271 (1996).
  - <sup>15</sup> N. D. Mermin, Phys. Rev. **137**, A1441 (1965).
  - <sup>16</sup> P. E. Blochl, O. Jepsen, and O. K. Andersen, Phys. Rev. B **49**, 16223 (1994).
  - <sup>17</sup> K. Kunc and R. M. Martin, Phys. Rev. Lett. **48**, 406 (1982).
  - <sup>18</sup> H. J. Deiseroth, O. Sommer, H. Binder, K. Wolfer, and B. Frei, Z. anorg. Allg. Chem. **571**, 21 (1989).
  - <sup>19</sup> I.Y. Kuznetsov, D.M. Vinitskii, K.A. Solntsev, N.T. Kuznetsov, and L.A. Butman, Russian J. Inorg. Chem. **32**, 1803 (1987).
  - <sup>20</sup> I. Tiritiris and T. Schleid, Z. anorg. Allg. Chem. **629**, 1390 (2003).
  - <sup>21</sup> T. Peymann, C. B. Knobler, S. I. Khan, and M. F. Hawthorne, J. Am. Chem. Soc. **123**, 2182 (2001).
  - <sup>22</sup> R. D. Dobrott and W. N. Lipscomb, J. Chem. Phys. **37**, 1779 (1962).
  - <sup>23</sup> O. Volkov, W. Dirk, U. Englert, and P. Paetzold, Z. Anorg. Allg. Chem. **625**, 1193 (1999).
  - <sup>24</sup> J. K. Kang, S. Y. Kim, Y. S. Han, R. P. Muller, and W. A. Goddard III, Appl. Phys. Lett. **87**, 111904 (2005).
  - <sup>25</sup> B. Morosin, A. W. Mullendore, D. Emin, and G. A. Slack, in *Boron-Rich Solids*, edited by D. Emin, T. L. Aselage, C. L. Beckel, I. A. Howard, and C. Wood, AIP Conf. Proc. No. 140 (AIP, New York, 1986), p. 70.
  - <sup>26</sup> R. B. King, I. Silaghi-Dumitrescu, and A. Lupan, Inorg. Chem. **44**, 7819 (2005).
  - <sup>27</sup> S. Orimo, Y. Nakamori, G. Kitahara, K. Miwa, N. Ohba, S. Towata, and A. Züttel, J. Alloys Comp. **404-406**, 427 (2005).
  - <sup>28</sup> S. Orimo, Y. Nakamori, N. Ohba, K. Miwa, M. Aoki, S. Towata, and A. Züttel, Appl. Phys. Lett. , to be published.
  - <sup>29</sup> G. Makov and M. C. Payne, Phys. Rev. B **51**, 4014 (1995).
  - <sup>30</sup> M. B. Smith and G. E. Bass Jr., J. Chem. Eng. Data **8**, 342 (1963).
  - <sup>31</sup> G. A. Olah, K. Wade, and R. E. Williams, *ELECTRON DEFICIENT BORON AND CARBON CLUSTERS*, (JOHN WILEY & SONS, 1991).